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Reaction of dialkyl phosphorous acids with aldehydes and ketones. IV.

Butyl and allyl esters of  $\alpha$ -hydroxyalkylphosphonic acids. (48-)

V. S. Abramov, R. V. Dmitrieva and A. S. Kapustina (Kazan Chem. Tech. Inst.).

Zhur. Obshch. Khim. 23, 257-62 (1953). Cf. this j. 23, 647 (1952).

Reaction of  $(RO)_2POH$  with aldehydes and ketones in the presence of  $RCNa$  yields addn. products of general type  $(RO)_2P(O)C(OH)R'R''$ , as evidenced by heat evolution on mixing the ingredients. However distn. of the reaction mixture generally leads to decompr. and isolation of starting materials; this is especially true for phosphites with large R units. (The text of the article is not clear, for statements concerning very ready isolation of the hydroxyphosphonates and the impossibility of their isolation are made side by side-C.M.K.). The reactions were run by addn. of a few drops of  $MeONa-MeOH$  to equimolar mixtures of dibutyl or diallyl phosphites and the desired carbonyl compound; after brief standing and/or heating the mixtures were distilled. The following were obtained:  $(BuO)_2P(O)CH(OH)Me$ , 56.7%, b<sub>9</sub> 162-3°, d<sub>4</sub><sup>20</sup> 1.024, n<sub>D</sub><sup>20</sup> 1.4384;  $(BuO)_2P(O)-CH(OH)Pr$ , 49%, b<sub>6</sub> 138-70°, d<sub>4</sub><sup>20</sup> 1.000, n<sub>D</sub><sup>20</sup> 1.4400;  $(BuO)_2P(O)CH(OH)CHMe_2$ , -%, b<sub>11</sub> 180-2°, d<sub>4</sub><sup>20</sup> 0.998, n<sub>D</sub><sup>20</sup> 1.4360;  $(BuO)_2P(O)CH(OH)Ph$ , -%, b<sub>6</sub> 168-70°, d<sub>4</sub><sup>20</sup> 1.026, n<sub>D</sub><sup>20</sup> 1.4680;  $(BuO)_2P(O)CMe_2OH$ , 59.2%, b<sub>7</sub> 154-5°, d<sub>4</sub><sup>20</sup> 1.018, n<sub>D</sub><sup>20</sup> 1.4366;  $(BuO)_2P(O)CHMeOH$ , 57.7%, b<sub>8</sub> 156-7°, d<sub>4</sub><sup>20</sup> 1.015, n<sub>D</sub><sup>20</sup> 1.4403;  $(BuO)_2P(O)CMePhOH$ , 30%, b<sub>9</sub> 179-80°, d<sub>4</sub><sup>20</sup> 1.025, n<sub>D</sub><sup>20</sup> 1.4670;  $(BuO)_2P(O)CPh OH$ , -%, b<sub>7</sub> 207-9°, d<sub>4</sub><sup>20</sup> 1.030, n<sub>D</sub><sup>20</sup> 1.4730;  $(BuO)_2P(O)C(OH)(CH_2)_4$ , 40.4%, b<sub>9</sub> 179-80°, d<sub>4</sub><sup>20</sup> 1.049, n<sub>D</sub><sup>20</sup> 1.4549;  $(BuO)_2P(O)C(OH)(CH_2)_5$ , 48.7%, b<sub>7</sub> 178-80°, d<sub>4</sub><sup>20</sup> 1.039, n<sub>D</sub><sup>20</sup> 1.4570;  $(CH_2:CHCH_2O)_2P(O)CHMeOH$ , 65.3%, b<sub>10</sub> 151°, d<sub>4</sub><sup>20</sup> 1.1187, n<sub>D</sub><sup>20</sup> 1.4565;  $(CH_2:CHCH_2O)_2P(O)CH(OH)Pr$ , 31.6%, b<sub>10</sub> 165-4°, d<sub>4</sub><sup>20</sup> 1.0769, n<sub>D</sub><sup>20</sup> 1.4552;  $(CH_2:CHCH_2O)_2P(O)CMe OH$ , 38.3%, b<sub>12</sub> 132°, d<sub>4</sub><sup>20</sup> 1.0907, n<sub>D</sub><sup>20</sup> 1.4500;  $(CH_2:CHCH_2O)_2P(O)C(OH)(CH_2)_4$ , 45.7%, b<sub>7</sub> 165-7°, d<sub>4</sub><sup>20</sup> 1.1253, n<sub>D</sub><sup>20</sup> 1.4740;  $(CH_2:CHCH_2O)_2P(O)C(OH)(CH_2)_5$ , -%, m. 56.5-7.0°.

Addn. of fra drops  $MeONa-MeOH$  to 9.7 g.  $(BuO)_2POH$  and either 4.3 g.  $MePrCO$ , 4.3 g.  $Et_2CO$  or 9.1 g.  $(PhCH_2)_2CO$  gave a temp. rise to 37-48°, then heated to 120-30° the reaction mixtures gave on attempted distn. only the startin-

materials. Reaction with iso-BuOClO gave similar results. Diallyl phosphite and iso-BuOClO also gave only starting materials, although the original reaction mixture appeared to give normal reaction; BuLi also failed to yield the desired ester with diallyl phosphite since during attempted distn, the mass decomposed at 170° yielding a foamy solid; only starting products were obtained from diallyl phosphite and either Et<sub>2</sub>CO or AcOH. Reaction of (BuO)<sub>2</sub>P(OH) with Et 2-ketocyclopentanecarboxylate (in presence of NaOMe) gave, after unstdtated period at 140-50° only small amounts of starting materials and much tar.

B  
Synthesis and properties of vinylphosphinic esters. I. Reaction of phosphonoethylation; addition of dialkyl phosphorous acids, ammonia and amines to ethyl ester of vinylphosphinic acid. 483

A. N. Pudovik and G. M. Denisova (Kazan State Univ.). Zhur. Obshchel Khim. 23, 263-7 (1955). Cf. this J. 28, 467 (1958).

To 8.3 g.  $\text{CH}_2=\text{CHP}(\text{O})(\text{OEt})_2$  (I) and 6.5 g. (MeO)<sub>2</sub>POH was added dropwise satd. MeOH-MeOHa, which resulted in vigorous reaction; after 24 hrs. at room temp. the mixt. was distd. yielding a little (MeO)<sub>2</sub>POH and 7.2 g.  $(\text{MeO})_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})(\text{OEt})_2$ ,  $b_2^{20}$  158-60°,  $n_D^{20}$  1.4430,  $d_4^{20}$  1.3075; similar reaction with (EtO)<sub>2</sub>POH in presence of EtCH-EtONa gave from 6 g. I 6.5 g.  $[\text{CH}_2(\text{PO}_2\text{Et}_2)]_2$ ,  $b_2^{20}$  164-5°,  $n_D^{20}$  1.4410,  $d_4^{20}$  1.1576; reaction with 4.0 g. I and 6.0 g. (BuO)<sub>2</sub>POH in presence of BuONa gave 5.3 g.  $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{OH}_2\text{P}(\text{O})(\text{OBu})_2$ ,  $b_2^{20}$  107-9°,  $n_D^{20}$  1.4430,  $d_4^{20}$  1.0631. Letting 10.4 g. I stand in 65 g. concd. THF-OH 24 hrs. gave after evapn. a glassy mass. Addn. of 7 g. I to 54.0 g. KOH contg. 10 g. NH<sub>3</sub> and letting the mixture stand 24 hrs. gave largely the starting materials. Repetition with 15 g. I in the presence of some MeOHa gave 11 g.  $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{NH}_2$ ,  $b_2^{20}$  95-5°,  $n_D^{20}$  1.4270,  $d_4^{20}$  1.05. Letting 5 g. I and 4.5 g.  $\frac{\text{Me}}{\text{NH}_3}$  stand overnight (spontaneous temp. rise) g.

0.8 g.  $(EtO)_2P(O)CH_2CH_2NH_2$ , b<sub>4</sub> 105-6°, n<sub>D</sub><sup>20</sup> 1.4345, d<sub>4</sub><sup>20</sup> 1.0157. Letting 10 g.  $(EtO)_2P(O)CH_2CH_2Br$ , 7.5 g.  $Na_2NH$  and 25 ml.  $N_2O$  stand 3 hrs., followed by addn. of 25 ml. 20% NaOH and extn. with  $C_6H_6$  gave 3.2 g. same ester, b<sub>4</sub> 108-9°, n<sub>D</sub><sup>20</sup> 1.4340, d<sub>4</sub><sup>20</sup> 1.0154. Letting 5 g. I and 3.7 g. piperidine stand 24 hrs. (only a weak reaction was evident) gave 4 g.  $(EtO)_2P(O)CH_2CH_2NOH_2$ , b<sub>3</sub> 155-7°, n<sub>D</sub><sup>20</sup> 1.0514, n<sub>D</sub><sup>20</sup> 1.4603; the same product was obtained from piperidine and  $(EtO)_2P(O)CH_2CH_2Br$ . Addn. of a little  $MeONa$  in  $MeOH$  to 7 g. I and 4 g.  $PhNH_2$  gave a temp. rise to 70°; after heating 1 hr. on a steam bath followed by 2 days standing there was isolated 1.5 g.  $(EtO)_2P(O)-CH_2CH_2NHPh$ , b<sub>3</sub> 145-50°, n<sub>D</sub><sup>20</sup> 1.4910, d<sub>4</sub><sup>20</sup> 1.0947, along with other fractions. Similar reaction with  $Ph_2NH$  failed to result in isolation of pure product.

II. Phosphonostylation reaction; addition of malonic, cyanoacetic, acetoacetic ester and their homologs to vinylphosphonic ester. 484

Shch A.N. Pudovik and O.N. Grishina. Ibid. 267-78.

Addn. of  $EtONa-EtOH$  over 10-15 min. until reaction ceased, to 0.5 g.  $(EtO)_2P(O)CH_2CH_2$  (I) and 10 g. di-Et malonate, followed by 1 hr. at room temp. gave 10.5 g. (70.5%),  $(EtO)_2P(O)CH_2CH_2(CO_2Et)_2$ , b<sub>3</sub> 155-9°, d<sub>4</sub><sup>20</sup> 1.1516, n<sub>D</sub><sup>20</sup> 1.4420; similarly were prep'd.: 78.9%  $(EtO)_2P(O)CH_2CH_2CO_2Et$ , b<sub>3</sub> 175-7°, d<sub>4</sub><sup>20</sup> 1.1021, n<sub>D</sub><sup>20</sup> 1.4400; 59.3%  $(EtO)_2P(O)CH_2CH_2C_2H_4(CO_2Et)_2$ , b<sub>3</sub> 165°, d<sub>4</sub><sup>20</sup> 1.0925, n<sub>D</sub><sup>20</sup> 1.4483; 78.4%  $(EtO)_2P(O)CH_2CH_2C_2H_4(CO_2Et)_2$ , b<sub>3</sub> 175-6°, d<sub>4</sub><sup>20</sup> 1.0782, n<sub>D</sub><sup>20</sup> 1.4455; 86.41%  $(EtO)_2P(O)CH_2CH_2CO_2Et(CO_2Et)_2$ , b<sub>3</sub> 155-6°, d<sub>4</sub><sup>20</sup> 1.0640, n<sub>D</sub><sup>20</sup> 1.4438. The products are insol. in  $N_2O$ . Slow addn. of  $EtONa-EtOH$  to 12 g. I and 3.2 g.  $EtO_2COCH_2CN$ , with periodic cooling, followed by distn. (some decompr.) gave 3.1 g.  $(EtO)_2P(O)CH_2CH_2\overset{CH}{C}(CN)CO_2Et$ , b<sub>3</sub> 155-7°, n<sub>D</sub><sup>20</sup> 1.4430, d<sub>4</sub><sup>20</sup> 1.0740, and 5.8 g.  $[(EtO)_2P(O)CH_2CH_2]_2C(CN)CO_2Et$ , b<sub>3</sub> 227°, n<sub>D</sub><sup>20</sup> 1.4540, d<sub>4</sub><sup>20</sup> 1.3550. Similarly were obtained: 88.9%  $(EtO)_2P(O)CH_2CH_2CO_2Et(CN)CO_2Et$ , b<sub>3</sub> 155-6°, d<sub>4</sub><sup>20</sup> 1.0989, n<sub>D</sub><sup>20</sup> 1.4430; 86.2%  $(EtO)_2P(O)CH_2CH_2C_2H_4CO_2Et$ .

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(CN)<sub>2</sub>Et, b<sub>3,5</sub> 166-7°, d<sub>4</sub><sup>20</sup> 1.0849, n<sub>D</sub><sup>20</sup> 1.4440; 83.7% (EtO)<sub>2</sub>P(O)CH<sub>2</sub>CH<sub>2</sub>O(CHMe<sub>2</sub>)<sub>2</sub>-  
(CN)<sub>2</sub>Et, b<sub>3</sub> 173-4°, d<sub>4</sub><sup>20</sup> 1.0702, n<sub>D</sub><sup>20</sup> 1.4443; 77.7% (EtO)<sub>2</sub>P(O)CH<sub>2</sub>CH<sub>2</sub>CBu(CN)-  
CO<sub>2</sub>Et, b<sub>3,5</sub> 177-8°, d<sub>4</sub><sup>20</sup> 1.0864, n<sub>D</sub><sup>20</sup> 1.4460. Addn. of 5.7 g. EtO<sub>2</sub>P(O)CH<sub>2</sub>CH<sub>2</sub>Br to  
0.93 g. Na in 14 ml. EtOH, followed by 10 g. (EtO)<sub>2</sub>P(O)CH<sub>2</sub>CH<sub>2</sub>Br, heating  
2 hrs. on steam bath, filtration and distn. gave 3.9 g. (EtO)<sub>2</sub>P(O)CH<sub>2</sub>CH<sub>2</sub>-  
CBr(CN)CO<sub>2</sub>Et, b<sub>4</sub> 167°, d<sub>4</sub><sup>20</sup> 1.4440, d<sub>4</sub><sup>20</sup> 1.0853, identical with above described.  
To 3.9 g. I and 6.4 g. AcCH<sub>2</sub>CO<sub>2</sub>Et was added satd. EtONa-EtOH; the reaction  
commenced only after addn. of 1-2 ml. of the catalyst soln.; after 1 hr. on  
a steam bath the mixture was distd. with considerable decompr. yielding  
2.85 g. (EtO)<sub>2</sub>P(O)CH<sub>2</sub>CH<sub>2</sub>CH(CO<sub>2</sub>Et)Ac, b<sub>4</sub> 170-2°, n<sub>D</sub><sup>20</sup> 1.4510. I (3.9 g.) and  
9.1 g. AcCH<sub>2</sub>CO<sub>2</sub>Et similarly gave 3.1 g. (EtO)<sub>2</sub>P(O)CH<sub>2</sub>CH<sub>2</sub>CPr(CO<sub>2</sub>Et)Ac,  
b<sub>4</sub> 156-41°, n<sub>D</sub><sup>20</sup> 1.4480. To 6.6 g. I and 4.9 g. PrCH<sub>2</sub>CN was added EtONa-EtOH,  
as above; distn. of the viscous illus. soln. gave 1.9 g. [(EtO)<sub>2</sub>P(O)CH<sub>2</sub>CH<sub>2</sub>]<sub>2</sub>C-  
PrCH<sub>2</sub>CN, b<sub>4</sub> 147-8°, n<sub>D</sub><sup>20</sup> 1.4940.

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